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Title of the Invention

ALUMINUM NITRIDE SINTERED BODY, PRODUCTION METHOD OF THE SAME,
AND APPARATUS FOR SEMICONDUCTOR FABRICATION

Abstract

The purpose of the present invention is to lower the lightness of an aluminum nitride sintered body and to make the color almost black without adding a metal compound, particularly a heavy metal compound, such as a sintering aid and a blackening agent to the aluminum nitride sintered body. Thus, in the x-ray diffraction chart of the main crystal phase of the aluminum nitride sintered body, there is another peak of carbon at an x-ray diffraction angle $2\theta = 44^\circ$ to 45° other than the peak of the aluminum nitride, the main crystal phase. Preferably, the crystal phase of the aluminum nitride sintered body comprises a main crystal phase of AlN, an auxiliary crystal phase ALON, and a carbon phase but practically no $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase and the lightness standardized by JIS Z 8721 is N4 or lower and the ratio of carbon atom contained in the aluminum nitride sintered body is 500 ppm to 5,000 ppm.

[What is claimed is:]

1. An aluminum nitride sintered body having a peak of carbon at an x-ray diffraction angle $2\theta = 44^\circ$ to 45° other than the peak of the aluminum nitride, the main crystal phase, in

the x-ray diffraction chart of the aluminum nitride.

2. The aluminum nitride sintered body as claimed in claim 1 having said main crystal phase, an auxiliary crystal phase ALON, and a carbon phase.

3. The aluminum nitride sintered body as claimed either claim 1 or claim 2 having practically no $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase and the lightness standardized by JIS Z 8721 is N4 or lower.

4. The aluminum nitride sintered body as claimed any of claims 1 to 3 having a ratio of carbon atom contained in the aluminum nitride sintered body in a range of 500 ppm to 5,000 ppm.

5. An apparatus for semiconductor fabrication comprising the aluminum nitride sintered body according to any of claims 1 to 4 as a substrate.

6. An aluminum nitride sintered body production method comprising a step of firing a raw material of an aluminum nitride powder having a carbon content of 500 ppm to 5,000 ppm at not lower than $1,730^\circ\text{C}$ and not higher than $1,920^\circ\text{C}$ in 80 kg/cm^2 or higher pressure to obtain the aluminum nitride sintered body.

7. The aluminum nitride sintered body production method as claimed in claim 6, wherein the method comprises a step of adding carbon or a compound to be a carbon source to an aluminum nitride powder so as to produce said raw material of an aluminum nitride powder having a carbon content of 500 ppm to 5,000 ppm.

8. The aluminum nitride sintered body production method

as claimed in claim 6, wherein the method comprises a step of mixing at least first and second kinds of aluminum nitride powders with different carbon contents so as to produce said raw material of an aluminum nitride powder having a carbon content of 500 ppm to 5,000 ppm.

9. The aluminum nitride sintered body production method as claimed in claim 8, wherein the method comprises a step of producing a second aluminum nitride powder by a reductive nitriding method.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an aluminum nitride sintered body and its production method and also relates to an apparatus for semiconductor fabrication using such an aluminum nitride sintered body as a substrate.

[0002]

[Prior Art]

In a semiconductor apparatus such as an etching apparatus, a chemical vapor deposition apparatus and the like, so-called a stainless heater and an indirect heating type heater have been common. However, in the case of using these heat sources, particles are sometimes produced attributed to the action of halogen-type corrosive gases and the heat efficiency is low. In order to solve such problems, applicants of the present

invention have disclosed a ceramic heater comprising a dense ceramic substrate and a high melting point metal wire embedded in the substrate (in JP Kokai Hei 3-261131). The wire is wound spirally in the inside of the disk-like substrate and connected to terminals at both ends. Such a ceramic heater has been found to be excellent especially for semiconductor fabrication.

[0003]

As a ceramic for composing the substrate of the ceramic heater, nitride-based ceramics such as silicon nitride, aluminum nitride, sialon and the like are supposed to be preferable. Further, in some cases, a susceptor is mounted on a ceramic heater and a semiconductor wafer is disposed on the susceptor to heat the semiconductor wafer. The applicants of the present invention have disclosed aluminum nitride is preferable as the substrate of such a ceramic heater and a susceptor (in JP Kokai Hei 5-101871). Especially in a semiconductor fabrication apparatus, halogen-type corrosive gases such as CF_3 or the like are used in many cases as an etching gas and a cleaning gas and that is because aluminum nitride has been confirmed to have remarkably high corrosion resistance in terms of the resistance to erosion by these halogen-type corrosive gases.

[0004]

[Problems to be Solved by the Invention]

However, an aluminum nitride sintered body itself has a characteristic that it generally has a white or white gray color.

However, a substrate to be used for a heater and a susceptor as described above is desired to be black. Because a substrate with black color radiate radiation heat in a high quantity and is excellent in the heating properties as compared with a substrate with white color. Further, regarding such kinds of products, in the case of using a substrate with white color or gray color, a fault that color of the surface of a product becomes uneven easily takes place and it is required to be improved. Further, in terms of user's preference, rather than a substrate with white or gray color, a substrate with a high blackness of black, dark brown, or dark gray color and a low lightness is desired. Moreover, the substrate with white or gray color is inferior in the radiation property.

[0005]

In order to blacken an aluminum nitride sintered body, it has been known that a proper metal element (a blackening agent) is added to a raw material powder and the powder is fired to produce a black aluminum nitride sintered body (in JP Application Publication Hei 5-64697). As the additive, tungsten, titanium oxide, nickel, palladium and the like are well known.

[0006]

However, if as a blackening agent, a metal element is added to an aluminum nitride sintered body in such a manner, the content of metal impurities in the aluminum nitride sintered body is naturally increased owing to the effect of the additives.

Especially in the semiconductor fabrication process, if group Ia elements, IIa elements, or transition metal elements exist in the aluminum nitride sintered body, even though the existing amount is slight, serious bad effects (for example, probable causes of defects of a semiconductor) would be caused on a semiconductor wafer and an apparatus itself. Therefore, it is required to decrease the lightness of the aluminum nitride sintered body without adding such a blackening agent as described above.

[0007]

The purpose of the present invention is to lower the lightness of an aluminum nitride sintered body and to make the color almost black without adding a metal compound, particularly a heavy metal compound, such as a sintering aid and a blackening agent to the aluminum nitride sintered body.

[0008]

[Means for Solving the Problems]

The present invention relates to an aluminum nitride sintered body having a peak of carbon at an x-ray diffraction angle $2\theta = 44^\circ$ to 45° other than the peak of the aluminum nitride, the main crystal phase, in the x-ray diffraction chart of the aluminum nitride.

[0009]

Further, the present invention relates to a semiconductor fabrication apparatus using the aluminum nitride sintered body

as a substrate. Further, the present invention relates to an aluminum nitride sintered body production method comprising a step of firing a raw material of an aluminum nitride powder having a carbon content of 500 ppm to 5,000 ppm at not lower than 1,730°C and not higher than 1,920°C in 80 kg/cm² or higher pressure to obtain the aluminum nitride sintered body.

[0010]

Inventors of the present invention have succeeded in producing an aluminum nitride sintered body with extremely low lightness and dark gray or dark brown color which scarcely contains metal elements such as blackening agents and the like other than aluminum and which particularly preferably is black with N4 or lower lightness standardized by JIS Z 8721.

[0011]

Since such an aluminum nitride sintered body showing black color with the lightness standardized by JIS Z 8721 of 4 or lower in a preferable embodiment, it radiates radiation heat in a high quantity and is excellent in heating characteristic. Accordingly, it is suitable for a substrate composing a heating material for a ceramic heater, a susceptor and the like. Moreover, since the content of metal elements other than aluminum can be decreased to an extremely low level, there is no probability to cause pollution in semiconductor and the like. Especially, in the semiconductor fabrication process, there is no probability to cause bad effects on a semiconductor wafer or an apparatus

itself. Further, color unevenness is scarcely outstanding in the surface of the aluminum nitride sintered body of the present invention to result in extremely excellent appearance of the aluminum nitride sintered body and moreover, since the blackness degree is high, the product value is remarkably improved.

[0012]

To explain practically, inventors of the present invention have made a raw material of an aluminum nitride powder with a carbon content of 500 ppm to 5,000 ppm and fired the raw material at a temperature of 1,730°C or higher in a pressure of 80 kg/cm² or higher by a hot press method and accordingly succeeded in producing an aluminum nitride substrate with low lightness and a dark brown or dark gray color as described above.

[0013]

The following methods are available for making the raw material of the aluminum nitride powder with a carbon content of 500 ppm to 5,000 ppm ready:

(1) the carbon content is adjusted to be 500 to 5,000 ppm by adding a prescribed amount of a carbon source to an aluminum nitride powder: and

(2) the raw material of the aluminum nitride powder with a carbon content of 500 ppm to 5,000 ppm is produced by mixing a plurality of kinds of aluminum nitride powders with different carbon contents. In this case, not less than three kinds of aluminum nitride powders can be mixed. In a preferable example,

the raw material of the aluminum nitride powder with a carbon content of 500 ppm to 5,000 ppm is produced by mixing a first aluminum nitride powder with a relatively low carbon content with a second aluminum nitride powder with a relatively high carbon content.

[0014]

In such a manner, by firing the aluminum nitride powder containing carbon in a prescribed ratio at a temperature within a prescribed range in a high pressure, the aluminum nitride sintered body with low lightness is successfully stably produced. In this case, if the carbon ratio is less than 500 ppm, the lightness of the sintered body becomes high and if it exceeds 5,000 ppm, the relative density of the aluminum nitride sintered body is lowered to less than 92% and its color tone becomes gray.

[0015]

Meanwhile, if the firing temperature is lower than 1,730°C, it is found that densification of the resulting sintered body becomes insufficient and that the aluminum nitride sintered body becomes white to result in increase of the lightness to 7 or higher. If the firing temperature of the above-mentioned powder exceeds 1,920°C, polycrystalline-type phase is produced and the lightness of the aluminum nitride sintered body is increased also in this case. In the case the firing temperature is within a range of 1,750 to 1,900°C, the lightness of the aluminum nitride sintered body is particularly decreased.

[0016]

Further, if the pressure is lower than 80 kg/cm^2 at the time of firing, it is found that the AlN-Al₂CO crystal phase is formed or polytype phase other than AlN crystal phase is formed to result in the increase of the lightness of the aluminum nitride sintered body. The pressure is preferably 150 kg/cm^2 or higher because of the reasons to be described later and more preferably 200 kg/cm^2 or higher. Nevertheless, the pressure is preferably controlled to be 0.5 ton/cm^2 in terms of the capability of a practical apparatus.

[0017]

The aluminum nitride sintered body further preferably has black color with N3 or lower lightness standardized by JIS Z 8721.

[0018]

Addition of metal elements other than aluminum to the raw material of the aluminum nitride powder should be avoided and their content is preferably suppressed to 100 ppm or lower. In this case, the metal elements other than aluminum include metal elements belonging to group Ia to VIIa, VIII, Ib, and IIb and some of elements (e.g. Si, Ga, Ge and the like) belonging to group IIIb, IVb.

[0019]

The word, lightness, will be described here. The surface color of an object is expressed as hue, lightness, and

chromaticness, which are three properties of the perceptive color. Among them, the lightness is a scale showing the visible property to determine the reflectance of the object surface is high or low. The scales of these three properties are standardized in JIS Z 8721. The lightness V is defined on the basis of the color with no chromaticness while setting the lightness of ideal black to be 0 and the lightness of ideal white to be 10. Between the ideal black and the ideal white, the respective colors are divided into ten degrees as to make the each lightness degree equal and denoted as symbols, N0 to N10. In the case of practical measurement of the lightness of an aluminum nitride sintered body, the surface color of the aluminum nitride sintered body is compared with the respective standard color chips corresponding to N0 to N10 to determine the lightness of the aluminum nitride sintered body. At that time, the lightness is determined basically to one place of decimal and the value of one place of decimal is set to be 0 or 5.

[0020]

The relative density of the aluminum nitride sintered body is a value defined by the following formula;
[relative density = bulk density/theoretical density] and the unit is [%].

[0021]

Further, inventors of the present invention have found that even in the case a hot isostatic press method under conditions

same as described above is employed, if the temperature and the pressure conditions are same as described above, a highly pure aluminum nitride sintered body with lightness of N4 or lower can be produced.

[0022]

Inventors of the present invention have made investigations of the reasons why the blackness is high and the lightness is low for the aluminum nitride sintered body obtained in the above-mentioned manner and consequently, have found the following facts and completed the present invention.

[0023]

That is, a specimen with dark brawn or dark gray color with lightness of 4N or lower contains AlN as a main crystal phase and ALON as an auxiliary crystal phase and no other crystal phase is found. Regarding the specimen, x-ray diffraction analysis makes it clear as shown in Fig. 1 that there is a clear peak for carbon appearing. That shows carbon phase is produced other than the above-mentioned AlN crystal phase and ALON crystal phase.

[0024]

Further, in the x-ray diffraction analysis chart, no peak corresponding to c-axis plane is detected. That means there exists a plane structure comprising only several stratified layers of carbon atom and accordingly, the thickness of carbon is extremely thin. The carbon is supposed to exist in the

periphery of grain boundaries of AlN crystal layers.

[0025]

When a specimen with such low lightness is thermally treated at, for example, 1,850°C under nitrogen atmosphere, as it will be understood from the x-ray diffraction chart shown in Fig. 2, although the AlN crystal phase remains, the peak for the ALON phase and carbon disappear and are not detected. That is supposedly attributed to the fact that oxygen and carbon in the ALON phase formed solid solution in the AlN crystal grains. For example, nitrogen site is replaced with oxygen atom to form a color center absorbing light with short waveform.

[0026]

The microstructure of the above-mentioned aluminum nitride sintered body of the present invention is shown in Fig. 3. Ultrafine ALON crystal exists in the AlN crystal grains and grain boundaries are hardly observed between the respective crystal phases and the boundary portions where the respective crystal grains are brought into contact with one another are dense and have no voids. Fig. 4 is an electron microscopic photograph showing a magnified crystal grain part of AlN of the aluminum nitride sintered body within the scope of the present invention and Fig. 5 is an electron microscopic photograph showing a magnified crystal grain part of AlN of a specimen with yellowish white. No different phase is observed among AlN crystal grains.

[0027]

A reductive nitriding method and a direct nitriding method are known as an aluminum nitride powder production method. In the present invention, in any case using a raw material powder produced by either one of these methods, an aluminum nitride sintered body with low lightness can be produced. The chemical formulas to be employed in the respective methods will be described below:

the reductive nitriding method; $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$

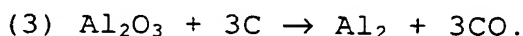
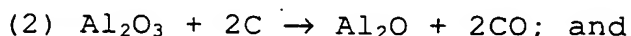
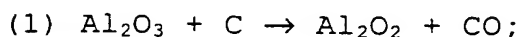
the direct nitriding method; $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{NH}_3 \rightarrow \text{AlN} + 3\text{C}_2\text{H}_6$ (gas phase process); and $2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN}$.

[0028]

At the time of firing an aluminum nitride powder, carbon in a prescribed ratio is added and the resulting powder is heated and fired in a high pressure and at that time, Al_2O_3 existing near the surface of the aluminum nitride powder is reduced by the added carbon to produce AlN. During the process promoted according to the following formulas (1), (2), and (3), a band continuously absorbing visible light in a wide range is supposedly produced to result in decrease of the lightness. However, at that moment, carbon phase should remain in the peripheries of the grain boundaries. When the firing temperature is increased high exceeding $1,950^\circ\text{C}$, it is supposed to take place that Al_2OC phase formation according to the reaction of $\text{Al}_2\text{O} + \text{C} \rightarrow \text{Al}_2\text{OC}$ proceeds and carbon phase is decreased and

accordingly the band of the surface of relatively unstable AlN particle produced according to the formulas (1), (2), and (3) is decreased. Meanwhile, in the case the retention time is too long, it is supposed that carbon is decreased in the same manner.

[0029]



[0030]

The aluminum nitride sintered body of the present invention generally comprises a main crystal phase of AlN, an auxiliary crystal phase of ALON, and carbon phase. In this case, it is especially preferable to contain practically no $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase and to have N4 or lower lightness standardized by JIS Z 8721.

[0031]

That is, when an aluminum nitride powder is fired in about 80 to 100 kg/cm² pressure, a gray aluminum nitride sintered body with lightness of 4 to 5 is sometimes produced. From the x-ray diffraction analysis results and other spectral analysis results of the crystal phase, its matrix is found composed of basically a main crystal phase of AlN, an auxiliary crystal phase of ALON, and carbon phase. Meanwhile, when 150 kg/cm² or higher pressure is employed, the lightness of the resulting sintered body is further decreased to stably obtain N4 or lower.

[0032]

Thus, no significant difference is found between the microstructures or the like of the basic matrices of both sintered bodies mentioned above. However, as shown in respective electron microscopic photographs of Fig. 6 and Fig. 7, it is made clear that a slight amount of $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase is formed in the gray product. In the periphery of the phase, fine voids are formed in the gap to the AlN crystal phase and light is diffused in the voids and thus the diffused light causes the increase of the lightness. Accordingly, the lightness of the aluminum nitride sintered body can be suppressed to 4 or lower, further to 3.5 or lower by preventing the formation of such $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase.

[0033]

As a carbon source to be added to the aluminum nitride powder, the following are preferably employed:

- (1) carbon-containing resin; e.g. scattering organic resin of an organic resin powder such as phenol resin powder;
- (2) a carbon powder of such as carbon black, graphite and the like; and
- (3) an intermediate product of aluminum nitride with a high carbon concentration produced during the reductive nitriding method or the like.

[0034]

As the method for mixing the aluminum nitride powder and

the carbon source, dry mixing methods using a dry bag mixing, a ball mill, a vibration mill and the like and wet mixing methods using organic solvents and the like can be employed.

[0035]

The aluminum nitride sintered body of the present invention is capable of radiating heat in a high radiation heat quantity and excellent in heating properties. Further, since it has dark brown or dark gray color while the color unevenness of the surface being scarcely outstanding, the product value is high. Therefore, it can especially preferably used for a variety of heating apparatuses. Further, since the aluminum nitride sintered body of the present invention is produced without using any sintering aid or a blackening agent to be a supply source of metals other than aluminum and thus have the content of each metal atom other than aluminum suppressed to 100 ppm or lower, there is not probability of contamination. Accordingly, the aluminum nitride sintered body of the present invention is suited for the materials for the highly purified process. Especially, in a semiconductor fabrication process, there is no probability of causing serious bad effects on a semiconductor wafer or an apparatus itself.

[0036]

An semiconductor fabrication apparatus employing the aluminum nitride sintered body of the present invention as a substrate includes positively functioning apparatus such as a

ceramic heater comprising a resistance heating element embedded in an aluminum nitride substrate, a ceramic electrostatic chuck comprising electrodes for an electrostatic chuck embedded in a substrate, a heater equipped with an electrostatic chuck and comprising a resistance heating element and electrodes for the electrostatic chuck both embedded in a substrate, an electrode apparatus for generating high frequency comprising electrodes for plasma generation embedded in a substrate and the like.

[0037]

Further, the apparatus also includes a variety of semiconductor fabrication apparatus such as a susceptor to mount a semiconductor wafer thereon, a dummy wafer, a shadow ring, a tube for generating high frequency plasma, a dome for generating high frequency plasma, a high frequency transmitting window, an IR transmitting window, a lift pin for supporting a semiconductor wafer, a shower plate and the like.

[0038]

The thermal conductivity of the aluminum nitride sintered body is preferably $90 \text{ W/m}\cdot\text{K}$ or higher for the use as a substrate for heating member such as a ceramic heater, a heater equipped with an electrostatic chuck, a susceptor for holding a semiconductor wafer and the like.

[0039]

[Example] (Experiment A)

Respective aluminum nitride sintered bodies of A1 to A12

shown in Table 1 and Table 2 were produced in the following manner. As aluminum nitride raw materials, highly pure powders produced by the reductive nitriding method and the direct nitriding method were used. Each content of Si, Fe, Ca, Mg, K, Na, Cr, Mn, Ni, Cu, Zn, W, B, and Y was suppressed to 100 ppm or less in the respective powders and no metal other than aluminum and these metals was detected. In the respective experimental examples, the carbon contents were as shown in Table 1 and Table 2.

[0040]

Disk-like preliminarily formed bodies were produced by uniaxially forming the respective raw material powders and fired by hot press in airtight state. The firing temperature, the holding duration at each firing temperature, and the pressure in this firing step were changed as shown in Table 1 and Table 2. Regarding the aluminum nitride sintered bodies of the respective examples, the main crystal phases and other crystal phases of the sintered bodies were measured by x-ray diffraction analysis. Further, the relative densities of the sintered bodies were calculated as the ratios of the bulk densities/the theoretical densities and the bulk densities were measured by Archimedes' principle. The theoretical densities of the sintered bodies were 3.26 g/cc since they did not contain any sintering aid with a high density. The carbon content in each sintered body was measured by spectroscopy. The color tone of each sintered body was measured by eye observation and the

lightness was measured as described above.

[0041]

[Table 1]

	Experiment A1	Experiment A2	Experiment A3	Experiment A4	Experiment A5	Experiment A6
AlN powder	Reductive nitriding	Reductive nitriding	Reductive nitriding	Reductive nitriding	Reductive nitriding	Reductive nitriding
Carbon content (ppm)	150	500	750	750	750	750
Firing temperature (°C)	1800	1800	1700	1750	1850	1800
Holding duration (hour)	2	1	2	2	2	3
Pressure (kg/cm ²)	200	100	200	150	50	200
Main crystal phase	AlN	AlN	AlN	AlN	AlN	AlN
Other crystal phase	ALON	ALON Carbon	ALON	ALON Carbon	ALON Carbon AlN-Al ₂ CO	ALON Carbon
Relative density (%)	99.5	98.0	97.0	98.5	97.0	99.5
Carbon content in sintered body (ppm)	150	500	740	750	750	750
Color tone of sintered body	Gray	Dark gray	White	Dark gray	Gray	Dark gray
Lightness of sintered body	N5.0	N3.5	N8.5	N4.0	N5.0	N3.0

[0042]

[Table 2]

	Experiment A7	Experiment A8	Experiment A9	Experiment A10	Experiment A11	Experiment A12
AlN powder	Direct nitriding	Reductive nitriding	Reductive nitriding	Reductive nitriding	Direct nitriding	Reductive nitriding
Carbon content (ppm)	750	750	1000	5000	5000	10000
Firing temperature (°C)	1930	1950	1800	1800	1800	1800
Holding duration (hour)	1	4	2	2	2	2
Pressure (kg/cm ²)	200	150	200	250	250	200
Main crystal phase	AlN	AlN	AlN	AlN	AlN	AlN
Other crystal phase	ALON Carbon	Polytype	ALON Carbon	ALON Carbon	ALON Carbon	ALON Carbon
Relative density (%)	95.0	99.5	97.0	95.0	92.0	90.0
Carbon content in sintered body (ppm)	750	700	950	4800	4900	9800
Color tone of sintered body	Dark gray	Milky white	Dark gray	Dark gray	Dark Gray	Gray
Lightness of sintered body	N4.0	N8.0	N3.5	N3.5	N4.0	N5.0

[0043]

In the experiment A1 out of the present invention, the carbon content was set to be 150 ppm, the firing temperature be 1,800°C, and the pressure be 200 kg/cm². Regarding the obtained sintered body, the crystal phase other than AlN crystal phase was only ALON and no carbon phase was detected by x-ray diffraction analysis. The color tone was gray color. In the experiment A2 within the present invention, the carbon content was set to be 500 ppm, the firing temperature be 1,800°C, and the pressure be 100 kg/cm². Regarding the obtained sintered body, ALON crystal phase and carbon phase were detected. The color tone of the sintered body was dark gray color and the lightness was N3.5. In the experiment A3 out of the present invention, the carbon content was set to be 750 ppm, the firing temperature be 1,700°C, and the pressure be 200 kg/cm². Regarding the obtained sintered body, no carbon phase was detected. The color tone of the sintered body was white.

[0044]

In the experiment A4 within the present invention, the carbon content was set to be 750 ppm, the firing temperature be 1,750°C, and the pressure be 150 kg/cm². Regarding the obtained sintered body, ALON crystal phase and carbon phase were detected. The color tone of the sintered body was dark gray color and the lightness was N4. In the experiment A5 within the present invention, the carbon content was set to be 750 ppm,

the firing temperature be $1,850^{\circ}\text{C}$, and the pressure be 50 kg/cm^2 . Regarding the obtained sintered body, $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase other than ALON crystal phase and carbon phase was detected. Although the color tone of the sintered body was gray color, as described above, blackening of the matrix was found significantly promoted. Excellent results were obtained also in the experiments A6, A7 within the present invention.

[0045]

In the experiment A8 which is out of the present invention, the carbon content was set to be 750 ppm, the firing temperature be $1,950^{\circ}\text{C}$, and the pressure be 150 kg/cm^2 . Regarding the obtained sintered body, the crystal phase other than AlN crystal phase was polytype. The color tone of the sintered body was milky white and the lightness was N8. Excellent results were obtained also in the experiments A9, A10, and A11 within the present invention. In the experiment A12 within the present invention, the carbon content was set to be 10,000 ppm, the firing temperature be $1,800^{\circ}\text{C}$, and the pressure be 200 kg/cm^2 . Regarding the obtained sintered body, carbon phase was formed and blackening of the matrix was significantly promoted. However, since the porosity was increased, the lightness of the entire sintered body became N5.

[0046]

Among the sintered bodies, the x-ray diffraction chart of the sintered body of the experiment A6 is shown in Fig. 1.

Respective peaks for AlN, AlNO, and carbon phases are confirmed. The microscopic photograph showing the ceramic structure of the sintered body of the experiment A6 is shown in Fig. 3 and the ceramic structure in the periphery of the grain boundary is shown in Fig. 4. Similar x-ray diffraction charts and crystal structures are observed for the sintered bodies of the experiments A2, A4, A7, A9, A10, and A11, respectively.

[0047]

Fig. 6 shows the ceramic structure of the sintered body of the experiment A5 and Fig. 7 shows a magnified figure of the ceramic structure. In the structure, the analysis results of the x-ray diffraction and the analysis results of the visible light absorption spectrum of the matrix portion are same as those of the experiment A6. However, in the matrix, there exists the $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase seen black and slight voids exist between this crystal grains and the AlN crystal phase and light is diffused in the voids to emit white luminance. The matrix structure of the sintered body is basically of the aluminum nitride sintered body of the present invention and blackening is relatively promoted. However, owing to the above-mentioned diffused light, the lightness of the sintered body was increased by that degree to be N5.

[0048]

Next, the experiment of thermal treatment of the sintered body of the above-mentioned experiment A6 in nitrogen atmosphere

was carried out. When the sintered body was heated at 1,850°C for 2 hours, only the outer circumferential portion of the sintered body was changed to be yellowish white and the color tone and the lightness of the center portion were not changed. From the analysis results of x-ray diffraction of the portions changed to be yellowish white, the main crystal phase was found to be AlN crystal phase and peaks of ALON phase and carbon disappeared and were not detected. No change was observed in the relative density and the lattice constant ratio.

[0049]

In the surface periphery of the sintered body of the experiment A6, oxygen in the nitrogen atmosphere, oxygen of the ALON phase, and also carbon are supposed to form a solid solution in the AlN crystal grains. In the inside of the sintered body, such reactions are supposed to proceed slowly.

[0050]

(Experiment B) In the same manner as the experiment A, the respective aluminum nitride sintered bodies of the experiments B1 to B15 shown in Table 3, Table 4, and Table 5 were actually produced. As the aluminum nitride raw materials, highly pure powders produced by the reductive nitriding method and the direct nitriding method were used. Each content of Si, Fe, Ca, Mg, K, Na, Cr, Mn, Ni, Cu, Zn, W, B, and Y was suppressed to 100 ppm or less in the respective powders and no metal other than aluminum was detected.

[0051]

In the experiment B1, an aluminum nitride powder (the carbon content of 500 ppm) obtained by the reductive nitriding method was used. In other experiments, to the aluminum nitride powders with the respective carbon contents, additives with relatively high carbon contents were added. As the additives, resin was used for some of the experiment examples and aluminum nitride powders with relatively higher carbon contents were used in the rest of the experiment examples. As the foregoing resin, a phenol resin powder was used and the addition amounts were shown. As the foregoing aluminum nitride powders, those produced by the reductive nitriding method were used and their carbon contents and addition amounts were shown. Further, the total carbon amounts (ppm) in the respective raw material powders after the mixing were shown.

[0052]

Disk-like preliminarily formed bodies were produced by uniaxially forming the respective raw material powders with pressure and fired with hot press in airtight state. The firing temperature, the holding duration at each firing temperature, and the pressure in this firing step were changed as shown in Table 3, Table 4, and Table 5. Regarding the aluminum nitride sintered bodies of the respective examples, the main crystal phases and other crystal phases of the sintered bodies were measured by x-ray diffraction analysis. Further, the relative

densities, the color tone, and the lightness of the sintered bodies were measured by the same methods as those in the experiment A.

[0053]

[Table 3]

	Experiment B1	Experiment B2	Experiment B3	Experiment B4	Experiment B5
AlN powder	Reductive nitriding 500	Reductive nitriding 400	Reductive nitriding 500	Reductive nitriding 700	Reductive nitriding 700
Carbon content	-	AlN powder 800	Resin 500000	AlN powder 1000	AlN powder 10000
Additive		50	-0.02	10	2.5
Carbon content Addition amount (% by weight)					
Total carbon amount	500	600	600	730	930
Firing temperature (°C)	1800	1800	1800	1750	1800
Holding duration (hour)	2	2	1	2	2
Pressure (kg/cm ²)	200	200	200	200	200
Main crystal phase	AlN	AlN	AlN	AlN	AlN
Other crystal phase	ALON	ALON	ALON	ALON	ALON
Relative density (%)	Carbon 99.4	Carbon 99.5	Carbon 99.6	Carbon 99.4	Carbon 98.5
Carbon content in sintered body (ppm)	500	600	600	720	920
Color · tone of sintered body	Dark gray	Dark gray	Dark gray	Dark gray	Dark gray
Lightness of sintered body	N4.0	N4.0	N4.0	N4.0	N4.0

[0054]

[Table 4]

	Experiment B6	Experiment B7	Experiment B8	Experiment B9	Experiment B10
AlN powder	Reductive nitriding 600	Reductive nitriding 500	Direct nitriding 400	Reductive nitriding 300	Reductive nitriding 300
Carbon content	Resin 500000	Resin 500000	AlN powder 10000	AlN powder 20000	AlN powder 20000
Additive	0.05	0.05	2.5	5	5
Carbon content Addition amount (% by weight)	850	750	640	1285	1285
Total carbon amount	1800	1650	1800	1800	1800
Firing temperature (°C)	2	1	1	80	70
Holding duration (hour)	200	200	250	150	100
Pressure (kg/cm ²)	AlN	AlN	AlN	AlN	AlN
Main crystal phase	ALON	ALON	ALON	ALON	ALON
Other crystal phase	Carbon	Carbon	Carbon	Carbon	Carbon
Relative density (%)	98.5	95.0	95.0	97.2	98.0
Carbon content in sintered body (ppm)	840	750	640	1270	1240
Color tone of sintered body	Dark gray	White	Dark gray	Dark gray	Gray
Lightness of sintered body	N4.0	N8.0	N4.0	N3.5	N5.0

[0055]

[Table 5]

	Experiment B11	Experiment B12	Experiment B13	Experiment B14	Experiment B15
AlN powder	Reductive nitriding 300	Reductive nitriding 300	Reductive nitriding 300	Reductive nitriding 1000	Reductive nitriding 4000
Carbon content	AlN powder 20000	Resin 500000	AlN powder 50000	AlN powder 40000	AlN powder 40000
Additive	5	0.2	3	10	10
Carbon content Addition amount (% by weight)					
Total carbon amount	1285	1299	1791	4900	7600
Firing temperature (°C)	1940	1800	1800	1800	1800
Holding duration (hour)	1	2	2	2	2
Pressure (kg/cm ²)	100	200	200	200	250
Main crystal phase	AlN	AlN	AlN	AlN	AlN
Other crystal phase	Polytype	ALON	ALON	ALON	ALON
Relative density (%)	98.0	Carbon 96.0	Carbon 97.0	Al ₂ OC 95.2	Carbon 88.0
Carbon content in sintered body (ppm)	1200	1280	1700	4500	7200
Color tone of sintered body	Milky white	Dark gray	Dark gray	Dark gray	Gray
Lightness of sintered body	N7.0	N3.5	N3.5	N3.5	N5.0

[0056]

In the experiment B1 of the present invention, an aluminum nitride sintered body with dark gray color was obtained. In any of the experiments B2, B3, B4, B5, and B6 within the present invention, aluminum nitride sintered bodies all with dark gray color tone were obtained. In the experiment B7 out of the present invention, since the firing temperature was as low as 1,650°C, densification of the sintered body did not proceed and no carbon phase was formed, so that the color tone of the sintered body became white. In the experiments B8 and B9 within the present invention, aluminum nitride sintered bodies with dark gray color tone were obtained. In the experiment B10 within the present invention, although the pressure was 70 kg/cm², carbon phase was formed in the obtained aluminum nitride sintered body and blackening of the matrix was promoted, however the lightness of the whole sintered body was increased. The ceramic structure of the sintered body comprised $(\text{AlN})_x(\text{Al}_2\text{OC})_{1-x}$ phase, which was seen black, existing in the matrix as same as the sintered body of the experiment A5 and slight voids existed between the crystal grains and the AlN crystal phase and light was diffused in the voids to emit white luminescence.

[0057]

In the experiment B11 out of the experiment, since the firing temperature was too high, the crystal phase other than the AlN crystal phase became poly type and the color tone of

the sintered body became milky white. In the experiments B12, B13, and B14 within the present invention, aluminum nitride sintered bodies with dark gray color tone were obtained. In the experiment B15 within the present invention, the total carbon amount in the entire aluminum nitride raw material powder was 7,600 ppm and as the crystal phase other than the AlN crystal phase, the ALON crystal phase and carbon phase were formed. However, since sintering of the sintered body did not proceed and the relative density reached only 88.0%, the lightness was N5.

[0058]

(Experiment of heating wafer)

A plate with a diameter of 210 mm and a thickness of 10 mm was made ready using the aluminum nitride sintered body produced by the experiment A6 of the present invention and the plate was disposed in a vacuum chamber equipped with a heating mechanism of IR lamps. A silicon wafer with a diameter of 8 inch was mounted on the plate and thermocouples for simultaneously measuring the respective temperatures of the plate and the silicon wafer were installed. As the IR lamps, twenty lamps having 500 W power and a peak of IR rays around 1 μ m wavelength were disposed and their reflection plate and the respective IR lamps were disposed at the outside of a vacuum chamber.

[0059]

IR rays radiated from the respective IR lamps were directly or after being reflected by the reflection plate transmitted through a circular quartz window (of 250 mm diameter and 5 mm thickness) formed in the vacuum chamber and reached the aluminum nitride plate and heated the plate.

[0060]

In the heating apparatus, the respective IR lamps were heated and the temperature of the plate was increased from a room temperature to 700°C in 11 minutes and kept at 700°C for 1 hour and after that, the IR lamps were turned off to gradually cool the plate. As a result, the power consumption of the IR lamps was at maximum 8,600 W and stable temperature control was possible. Further, the temperature of the silicon wafer was measured and when the temperature of the plate was kept at 700°C, the temperature of the silicon wafer was 611°C.

[0061]

When similar experiments were carried out for the aluminum nitride sintered bodies of the experiments A2, A9, A10, and A11, the results similar to those described above were obtained.

[0062]

(Experiment of heating by comparative example)

Next, using an aluminum nitride powder having a carbon content of 750 ppm and obtained by the reductive nitriding method, a disk-like formed body was produced by pressurizing the powder in 3 ton/cm² by a cold isostatic press method and the formed

body was fired at 1,900°C for 2 hours to produce a white aluminum nitride sintered body with a density of 99.4%. Using the sintered body, a heating experiment of a silicon wafer was carried out in the same manner as described above.

[0063]

Consequently, the power consumption became at the maximum 10 kW and about 2 minute-delay was observed regarding the temperature increase time. Further, when the heating cycles of temperature increase and decrease between the room temperature and 700°C were repeated in the above-mentioned manner, the IR lamps were found easily disconnected. Also, in the case the temperature of the silicon wafer was measured, during the time the plate was being kept at 700°C, the temperature of the silicon wafer was 593°C and as compared with that in the above-mentioned example, the temperature of the silicon wafer was found also decreased.

[0064]

(Experiment of embedding electrode and resistance heating element)

In the same manner as the experiment A6 of the present invention, an aluminum nitride powder having a carbon content of 750 ppm and produced by the reductive nitriding method was made ready and in this powder, a coil (a resistance heating element) of a wire having a diameter of 0.5 mm and made of molybdenum was embedded and column-like electrodes having a

diameter of 5 mm and a length of 10 mm and made of molybdenum were connected with the wire and embedded. The resulting embedding unit was formed by uniaxial press-forming to obtain a disk-like formed body. At that time, the plane view shape of the embedded coil in the formed body was made to be spiral.

[0065]

The disk-like formed body was held at 1,800°C for 3 hours in 200 kg/cm² pressure by hot press method to obtain an aluminum nitride sintered body. In the obtained aluminum nitride sintered body, the above-mentioned resistance heating element and the molybdenum electrodes were embedded. The molybdenum electrodes could be used as electrostatic chuck electrodes and also electrodes for high frequency.

[0066]

[Effects of the Invention]

As described above, according to the present invention, the lightness of an aluminum nitride sintered body can be lowered and the color can be made almost black without addition of any sintering aid or a blackening agent of such as a metal compound, especially a heavy metal compound, to aluminum nitride.

[Brief Description of the Drawings]

[Fig. 1] A chart showing the x-ray diffraction analysis of an aluminum nitride sintered body according to an example of the present invention.

[Fig. 2] A chart showing the x-ray diffraction analysis of an

aluminum nitride sintered body according to a comparative example.

[Fig. 3] An electron microscopic photograph showing the ceramic structure of an aluminum nitride sintered body according to an example of the present invention.

[Fig. 4] An electron microscopic photograph showing the ceramic structure in the periphery of grain boundary of AlN crystal phase in an aluminum nitride sintered body according to an example of the present invention.

[Fig. 5] An electron microscopic photograph showing the ceramic structure in the periphery of grain boundary of AlN crystal phase in an aluminum nitride sintered body according to a comparative example.

[Fig. 6] An electron microscopic photograph showing the ceramic structure in the state that grains of $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase are formed in the matrix of the grains of AlN crystal phase.

[Fig. 7] An electron microscopic photograph of the ceramic structure in which the matrix and grains of $(\text{AlN})_x(\text{Al}_2\text{O}_3)_{1-x}$ phase of Fig. 6 are shown while being magnified.

[Fig. 1] [Fig. 2]

photograph substitutes for drawing

[Fig. 3] - [Fig. 7]

longitudinal axis: Intensity

6)